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## (54) "MICROCAPSULES CONTAINING DYES"

- (71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The invention relates to dye-containing microcapsules for use in copying paper and also copying paper comprising a substrate having on a surface thereof a coating comprising such microcapsules.
- 15 It is known that microcapsules containing dye can be used for carbonless copying paper, the pressure applied in writing or typing generally rupturing the microcapsules and transferring the dye released to a receptive material, or
- 20 when a leuco compound is used, developing the actual dye on the receptive material.
- To form the dye on the receptive material a solvent is necessary because generally the dye can only be adsorbed onto the receptive material
- 25 by way of its dissolved form.
- Examples of solvents which have been described for the dyes and which at the same time are solvents for the dyes and core materials for the microcapsules are: hydrocarbons such as
- 30 petroleum distillate, xylenes, diphenyls and/or chlorinated compounds. The solvents conventionally used are almost exclusively mixtures of chlorinated hydrocarbons, particularly a mixture of chlorinated diphenyls. These chlorinated
- 35 compounds have a number of disadvantages; because of their high densities the microcapsule dispersions settle out fairly easily and form agglomerates so that problems arise in storage, metering or processing into paper
- 40 coating material.
- Chlorinated diphenyls also have the disadvantage that development of the dye takes place fairly slowly in their presence. It is also known that particularly the chlorinated diphenyls have a certain toxicity, are not de-
- gradable chemically or microbiologically and may accumulate in certain organs of living organisms. Residues can only be completely removed by burning, which involves the formation of troublesome hydrogen chloride gas.
- 50 When the paper is reused as waste paper there is a risk that the said substances may pass into foodstuffs via packaging materials. They also have an unpleasant odor.
- There is therefore a demand for new solvents (hereinafter also referred to as developer liquids) as core materials for microcapsules containing dyes.
- 55 The invention provides microcapsules containing as microencapsulated material at least one dye and a water-immiscible liquid which comprises one or more monoalkyl-substituted benzenes of which the alkyl group contains at least five carbon atoms or one or more poly-
- 60 alkyl-substituted benzenes of which the alkyl groups are, each independently, linear or branched and contain, each independently, from one to eighteen carbon atoms with the alkyl groups containing a combined total of at least five carbon atoms.
- 70 Examples of suitable alkyl radicals are: hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl.
- The following are examples of suitable 75 branched alkyl radicals: neopentyl (= 2,2-dimethylpropyl), isohexyl (= 2-ethylbutyl) secbutyl, tert-butyl, and isopropyl.
- In the case of monoalkylbenzenes those of 80 which the alkyl radical contains ten or more carbon atoms, for example from 10 to 18 carbon atoms, are particularly suitable.
- The polyalkyl-substituted benzenes may also contain lower alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, 85 sec-butyl or amyl. In disubstituted benzenes the radicals may be in the ortho-, meta- or para-position; in the case of trisubstituted benzenes the radicals may be arranged in symmetric, asymmetric or vicinal position, in the case of 90

tetrasubstituted benzenes the radicals may be in the positions 1,2,4,5 or 1,2,3,4 or 1,2,3,5. The total number of carbon atoms of all the alkyl radicals should always be at least five.

5 Naturally polyalkylated benzenes may contain one or more lower alkyl radicals as well as one or more long-chain alkyl radicals. In the present context long-chain alkyl radicals are those having from eight to eighteen carbon atoms and lower alkyl chains as those having one to

10 seven carbon atoms.

The monoalkyl-substituted or polyalkyl-substituted benzenes have advantageous properties as developer liquids or solvents for reactive dyes. They have fairly high boiling points and particularly in the form of mixtures they have very low setting points of less than  $-50^{\circ}\text{C}$ . They have low viscosity over a wide range of temperatures and permit good transference of the dye to the receptive layer. The dye may even be fully developed in the solvent-wet condition of the receptive layer because the nonpolarity of the alkyl-substituted benzenes does not affect the adsorption and reaction of the dye on the acidic receptive layer.

It is surprising that a 6% by weight "solution" of for example a mixture of 3 parts of crystal violet lactone and 1 part of N-benzoylleucomethylene blue in diisopropylbenzene which contains only 1.76% by weight in solution or in n-dodecylbenzene which contains only 0.85% by weight in solution (the remainder of the dye-forming component remaining undissolved in each case) should result in a color intensity equal to that given by a 6% by weight solution in chlorinated diphenyl of the said dye-forming mixture. It has always been thought that only those solvents which have outstanding solvent power for the dye-forming component and ensure complete solution will guarantee a satisfactory dye development.

Since a surprisingly good dye development is achieved for example in the case of carbonless copying papers with microcapsules containing dyes and monoalkyl-substituted or polyalkyl-substituted benzenes as core material in spite of the rather poor solvent power which they have for reactive dyes, the term developer liquid is preferred to the term solvent in the following description. The function of the developer liquid is to convey the dissolved or undissolved dye-forming component to the point of dye development.

It is known from U.S. Patent 3,627,581 that a solvent for reactive dyes consisting of diphenyl and isopropylidiphenylene may have added to it mono- $\text{C}_{10}$  to  $\text{C}_{15}$ -alkylbenzenes up to two thirds of the total mixture. It is surprising however and is the merit of the invention that monoalkyl-substituted and polyalkyl-substituted benzenes alone, in spite of their fairly poor solvent power for reactive dyes, have been found to be outstanding developer liquids for the dye-forming components in carbonless copying papers.

On page 12 of German Laid-Open Specification No. 2,130,846 it is disclosed that higher alkylbenzenes such as dodecylbenzene, decylbenzene and octylbenzene are solvents for certain fluoran dyes which are suitable for pressure-sensitive copying papers. It is clear from the description (page 3) that satisfactory copying papers can only be prepared when the dye forming component has good solubility, i.e. is completely soluble in the solvent used.

Another advantage of alkyl-substituted benzenes over dichloro-diphenyl is that they have practically no solvent or softening effect on the polymeric wall material of the capsules so that in spite of the lower boiling point as compared with chlorodiphenyls the walls of the capsules remain impervious. For this reason for example copying papers can be prepared which will store better. The alkylbenzenes used are moreover substantially nontoxic and may be practically completely degraded biologically, particularly if a long unbranched alkyl chain is present. They are therefore much less harmful to the environment than the solvents hitherto used. Another advantage of the developer liquids is that their density is only slightly less than 1, so that stable aqueous capsule dispersions are obtained which are much simpler to store and easy to process. They are also good solvents for conventional ultraviolet absorbers, as for example Tinuvin P, ("TINUVIN" is a Registered Trade Mark), so that light stabilization of encapsulated dye-forming component offers no problems.

It is not necessary to use the alkylbenzenes as pure compounds. Mixtures of alkylbenzenes such as are formed for example in industrial alkylations may equally well be used. The mixtures have the advantage over the pure substances that they have lower pour points.

The following are examples of monosubstituted alkylbenzenes: pentylbenzene, hexylbenzene, heptylbenzene, octylbenzene, decylbenzene, dodecylbenzene, neopentylbenzene, (2-ethylbutyl)-benzene, tridecylbenzene and tetradecylbenzene.

The following are examples of disubstituted alkylbenzenes: 1-methyl-2butylbenzene, 1-methyl-2-hexylbenzene, 1-methyl-3-butylbenzene, 1-methyl-4-(1,1-dimethylpropyl)-benzene, 1,4-disecbutylbenzene, 1-methyl-4-tetradecylbenzene, 1,2-diisopropylbenzene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, dioctylbenzene and 1-methyl-4-tert-butylbenzene.

The following are examples of trisubstituted alkylbenzenes: 1,2-dimethyl-4-isopropylbenzene, polyethylbenzenes having at least three groups such as 1,3,5-triethylbenzene, 1-methyldipropylbenzene with any position of the propyl groups, 1,3-dimethyl-5-isopropylbenzene, 1,2,4-triisopropylbenzene, 1,2-dimethyl-3-butylbenzene and 1,3-dimethyl-5-(1,1-dimethylpropyl)-benzene.

The following are examples of tetrasubstituted alkylbenzenes: 1,2,4,5-tetraethylben-

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zene, 1,4-dimethyl-2,5-diisopropylbenzene. 1, 2,4-trimethyl-5-isopropylbenzene and 1,3,5-trimethyl-2-ethylbenzene. Tetraalkyl-substituted benzenes are expediently mixed with the above-mentioned alkylbenzene when the setting points of the mixtures are below  $-20^{\circ}\text{C}$ .

Preferred alkylbenzenes include:

diisopropylbenzenes, triisopropylbenzenes, polyethylbenzenes having at least three ethyl groups and particularly dodecylbenzene which is obtainable under various trade names, for example Marlikan, Korenyl and Dobane.

In further preferred embodiments the alkyl-substituted benzenes to be used according to the invention are advantageously used mixed with one another. Useful mixtures include: diisopropylbenzene and n-dodecylbenzene; triisopropylbenzene and n-dodecylbenzene; hexyltoluene and triisopropylbenzene; and polyethylbenzene and n-dodecylbenzene in ratios of from 1:5 to 5:1, particularly from 1:3 to 3:1.

Mixtures of more than two components include for example octylbenzene, decylbenzene, dodecylbenzene and tetradecylbenzene. Mixtures of  $\text{C}_8$ - $14$ -alkyl monoalkylbenzenes which contain up to 35%, particularly from 5 to 35%, by weight of the individual alkylbenzenes are especially advantageous.

The mono- or polyalkyl-substituted benzenes may obviously also be used mixed with up to 50% of other solvents which have been described as solvents for reactive dyes such as diphenylbenzenes (terphenyls), dialkyl phthalates, dicyclohexylbenzenes and unsubstituted or substituted indans and tetralins. Such compounds, as for example the alkylated indans and tetralins, may already be present in the alkylbenzenes used as byproducts from their production. Mixtures which do not contain more than 25% of other solvents, i.e. which contain at least 75% of monoalkyl-substituted or polyalkyl-substituted benzenes, are preferred.

Larger amounts of additional solvents are often less advantageous because they may too greatly increase the viscosity of the developer liquid and this in turn may impair color development.

Examples of mixtures with other solvents are mixtures of diisopropylbenzenes with diphenylbenzene; of diisopropylbenzene with dioctyl phthalate; of diisopropylbenzene with didodecylphthalate; of n-dodecylbenzene with p-diphenylbenzene, m-diphenylbenzene or o-diphenylbenzene, or of dodecylbenzene with dihexyl phthalate.

Aliphatic hydrocarbons such as high boiling point petroleum distillate and polynuclear aromatics which may be alkylated as for example alkylnaphthalenes are also suitable as mixing components for the alkyl-substituted benzenes.

Suitable dyes are those which have a solubility of at least 0.1% by weight in the developer liquid. In the case of the higher concentrations of dye-forming component some of the same be present in the developer liquid in undissolved

form. The reactive dyes known and conventionally used for copying papers such as crystal violet lactone, N-benzoylleucomethylene blue, 3-methyl-bis-naphthospiropyran, malachite green lactone, Rhodamine B lactone, o-hydroxybenzalacetophenone and fluorans are particularly suitable. These dyes and their use for copying papers are described for example in German Patent 671,604, German Printed Application DAS No. 1,183,918, U.S. Patents 3,179,600, 2,505,470, 2,505,472 and 2,505,480 and Japanese Patent Application No. 25,657/1970.

The microcapsules which contain the dyes and the alkylated benzenes or their mixtures as core material may be prepared by widely different methods and with a great variety of wall materials such as are known in the art. For example they may be prepared by complex coacervation such as is described in German Printed Application DAS No. 1,122,495 or by interfacial polymerization such as is described in German Laid-Open Specification DOS No. 1,444,415, or with urea-formaldehyde polycondensation products according to German Printed Application DAS No. 1,290,799. An atomizing method for the production of microcapsules is described in German Printed Application DAS No. 1,294,932, a gelling method of emulsion droplets in German Laid-Open Specification DOS No. 1,619,808 and a phase inversion method in German Laid-Open Specification DOS No. 1,912,323.

In a preferred method for the production of microcapsules a mixture containing the wall material, the reactive dye and the alkylated benzene mixture dissolved in a volatile organic solvent is dispersed in an aqueous carrier liquid and the wall material is desposited at the phase interface of the dispersed phase by evaporating the solvent.

A preferred wall material for this method is a copolymer obtained by solution polymerization of a mixture having the following composition:—

20 to 70% by weight of methyl methacrylate;  
20 to 70% by weight of an acetylacetate of a monoacrylate or

monomethacrylate of an aliphatic diol of two to eight carbon atoms such as butanediol-1-acrylate-4-acetyl-acetate;

0 to 30% by weight of acrylamide;  
0 to 30% by weight of acrylic or methacrylic acid;

0 to 30% of vinylpyrrolidone;  
0 to 3% by weight of vinylsulfonic acid or a salt thereof and

0 to 3% by weight of 2-sulfoethyl methacrylate or a salt thereof; as a rule of a K value of from 10 to 70 measured according to H. Fikentscher, *Cellulosechemie*, 13, 58 et seq. (1932).

This crosslinkable copolymer, as is evident from the Examples, is outstandingly suitable as wall material for microcapsules containing monoalkyl-substituted or polyalkyl-substituted benzenes or mixtures of the same and reactive dyes.

Suitable volatile solvents for the wall and core materials in this process are aliphatic chlorinated hydrocarbons such as chloroform or methylene chloride, with or without the addition of a lower aliphatic alcohol such as ethanol, propanol or isopropanol.

Examples of advantageous wall materials in other methods of production are gelatins, polyvinyl alcohol, urea-melamine resins, phenol-formaldehyde resins, polyamides and polyurethanes.

For the production of copying papers, the microcapsules obtained are as a rule applied as dispersions to a carrier material such as paper sheets or plastics film and dried. They may also for example be embedded in paper pulp or similar compositions consisting of other polymers. Because of their high density they may also be applied direct to conventional receptive layers. Examples of suitable receptive layers are kaolin, attapulgite, bentonite, acid colloidal silicon dioxide, zeolite and organic acid resins such as phenolic resins.

The following Examples illustrate the invention. The part and percentages specified are measured on a weight basis.

#### EXAMPLE 1

Production of the copolymer to be used as wall material:

500 parts of a mixture of 400 parts of butanediol monoacrylate acetylacetate, 395 parts of methyl methacrylate, 200 parts of acrylamide and 5 parts of the sodium salt of 2-sulfoethyl methacrylate which has previously been neutralized to pH 4 with 10% caustic soda solution, 7.5 parts of azobisisobutyronitrile and 1000 parts of isopropanol are placed in a stirred flask having a constant-temperature bath and heated to 80°C. Fifteen minutes after polymerization has started the remainder of the mixture is introduced uniformly over an hour into the reaction mixture at from 80° to 85°C. Polymerization is continued at the said temperature for three hours, the reaction mixture is cooled to room temperature and the polymer solution is diluted with 500 parts of chloroform so that a 37.7% by weight polymer solution is obtained. A 1% by weight solution in chloroform gives a K value of 36.3 for the polymer.

Production of the microcapsule dispersion:

60 parts of the solution of wall material thus prepared is dissolved together with 67 parts of p-diisopropylbenzene having a melting point of -17°C, 116 parts of chloroform, 0.5 part of tributylamine, 1 part of N-benzoylleucomethylene blue, 3 parts of 3,3-bis-(dimethylamino)-6-dimethylaminophthalide (crystal violet lactone) and 6 parts of isopropanol with stirring to make a homogeneous solution.

200 parts of water and 50 parts of a 10% solution of a polyvinyl-pyrrolidone of a K value of 90 are placed in a vessel holding 800 parts into which projects an Ultraturrax T45 stirrer (manufactured by Jahnke & Kunkel) rotating at 10,000 rpm. The above solution is then

added within about five minutes. Dispersion is continued until the mean particle size is from 10 to 12 microns. The temperature rises to about 45°C. An emulsion which is stable for a long period is obtained.

250 parts of water is placed in a stirred flask holding 2000 parts, the flask having a flat paddle agitator (120 rpm) and being fitted with a descending condenser and the emulsion obtained above is introduced while stirring. The chloroform is distilled off over about seventy-five minutes from the emulsion diluted in the said manner. The dispersion thus heated to 80°C has 7 parts of 40% formaldehyde solution added to it for hardening and the mixture is kept at 70°C for about another hour.

After cooling a yield of more than 98% of a stable dispersion is obtained which contains capsules having a mean diameter of from 10 to 15 microns. The capsules may readily be given free-flowing characteristics by filtration, repeated washing with water to remove the protective colloid and then drying. They are recovered most simply by spraying with simultaneous drying.

Testing the capsules for imperiousness:

Paper having a dry weight of 5.5 g/m<sup>2</sup> is stretched whilst moist on a frame and then dried. The microcapsule dispersion is then applied to the dried paper using a fine hair brush and the coating is then dried at room temperature. The dried coating amounts to 6 grams of microcapsule per square metre of paper. The papers so obtained are odorless.

Some of the coated paper so obtained is stored at room temperature, some at 80°C and some at 95°C for 16 hours in each case. After having been stored the papers are laid with their coated sides face down on a paper whose surface has been coated in the usual way with an acid bentonite as a receptive layer for the dye. The sheets of paper are inserted in a Triumph Electric 31 electric typewriter and typing is effected with the impact adjustment central of the typewriter at the position marked "2".

The copying characteristics of the coating are then evaluated using the following scale:

5 = intense blue, very sharp type, very easily read;

4 = strong blue, very easily read;

3 = blue, quite easy to read;

2 = bluish, only just legible;

1 = no coloration, no copy, illegible.

The coated paper which has been stored at room temperature immediately gives a blue copy (5). The paper stored at 80°C or at 95°C also immediately gives a copy of the same intensity (5). The experiment shows that the wall of the capsules is so impervious that in spite of being stored at elevated temperature the copying quality of the paper remains unchanged so that copying paper which can be stored for long periods at room temperature can be prepared with these capsules.

### Comparative Example 1a

The capsules are prepared by the procedure described in Example 1 except that 90 parts of dichlorodiphenyl and 10 parts of petroleum distillate (boiling range 155° and 180°C) are used instead of 67 parts of p-diisopropylbenzene. The amount of chloroform is decreased to 180 parts and the isopropanol is omitted.

A dispersion is obtained in a yield of more than 97% having capsules of a mean diameter of from 7 to 10 microns which very rapidly settles and gives a solid sediment.

A paper prepared in the same way with a coating of capsules of from 7 to 8 g/m<sup>2</sup> gives in the copying test in the typewriter a copy having a rating of 5 not only in the sample stored at room temperature but also in those stored at 85°C and at 95°C.

When the papers are stored in a large pile, a distinct odor of dichlorodiphenyl is noticeable when some of the paper is removed from the pile.

### Comparative Example 1b

The procedure for the production of the capsules described in Comparative Example 1a is repeated but 67 parts of xylene is used instead of the dichlorodiphenyl and mineral spirit.

A stable dispersion with capsules of a diameter of from 7 to 8 microns is formed in a yield of 98%.

A paper coated in the same way with 6 g/m<sup>2</sup> of capsules gives blue copies of intensity rating 3 in the typewriter after having been stored at room temperature. Neither the paper stored at 80°C nor the paper stored at 95°C gives any copy (rating 1). There has been so great a loss of xylene in storage that the dye-forming component can no longer be transferred to the receptive layer.

### EXAMPLE 2

(a) A core material consisting of 67 parts of polyethylbenzene (as obtained as a byproduct in the alkylation of benzene to ethylbenzene), 3 parts of crystal violet lactone and 1 part of N-benzoylleucomethylene blue is encapsulated according to Example 1 with the copolymer prepared as in Example 1 as well material, but only 180 parts of chloroform is added and no isopropanol.

A dispersion having capsules of a mean diameter of from 6 to 7 microns is obtained in a yield of more than 98%.

Papers are prepared therewith as described in Example 1 and after they have been stored at various temperatures their copying characteristics are tested. Paper stored at room temperature gives a rating of 4 and samples stored for sixteen hours at 80°C and at 95°C give intensities of rating 3. The copy is quite easily legible in each case.

(b) 67 parts of isopropylbenzene is used as developer liquid instead of the polyethylbenzene of Example 2 (a) and encapsulation is carried out. A stable dispersion forms in a yield of more than 98% having a mean capsule

diameter of from 5 to 7 microns.

Paper prepared therewith and stored at room temperature has a copying intensity of rating 5, while samples stored at 80°C and at 95°C give ratings of 2. The text can only just be read. When 40 parts of the isopropylbenzene is replaced by n-dodecylbenzene, the copy stored at room temperature is unchanged. Samples stored at 80° and at 95°C are raised to ratings of 5 and 4, respectively. The experiment shows that an alkylbenzene of three carbon atoms in the alkyl group is not suitable by itself for the production of storable copying paper.

For the following experiments a copolymer is prepared from 47.5 parts of butanediol monoacrylate acetylacetate, 38 parts of methyl methacrylate, 14 parts of acrylamide and 0.25 part of 2-sulfoethyl methacrylate. The K value measured according to Fikentscher in 1% solution in chloroform is 40.3.

(c) An n-dodecylbenzene is used as developer liquid for the dye-forming component instead of the polyethylbenzene in Example 2(a). The n-dodecylbenzene is obtained by industrial alkylation of benzene and is of the type used for the production of n-dodecylbenzenesulfonates. It consists of a mixture of isomers having alkyl substituents of ten to fourteen, mainly eleven to thirteen, carbon atoms and has a content of about 14% of alkylated indans and tetralins and a setting point of -70°C.

198 parts of chloroform and 1.2 parts of isopropanol are added to produce the solution. A stable dispersion is formed in a yield of more than 98% with capsules of a mean diameter of from 6 to 8 microns.

Paper coated with the capsules obtained is completely odorless after prolonged storage in a pile. The papers give copies of intensity rating 5 after storage at room temperature. The intensity does not change after storage for sixteen hours at 80° and at 95°C.

(d) Example 2(c) is varied by using only 1.5 parts of crystal violet lactone and 0.5 part of N-benzoylleucomethylene blue as dye-forming component. A stable dispersion is formed having a mean capsule diameter of from 7 to 8 microns.

Copies have an intensity rating of 4 irrespective of the temperature.

(e) Example 2(c) is varied by using 67 parts of 1,3,5-triisopropylbenzene as developer liquid instead of dodecylbenzene. 2 parts of Tinuvin P is added for light stabilization.

A stable dispersion is formed with a mean capsule diameter of from 8 to 10 microns.

Copying gives rating 5 for paper stored at room temperature and rating 4 for paper stored at 80° and at 95°C.

### EXAMPLE 3

As described in Example 1 a developer liquid consisting of 40 parts of n-dodecylbenzene and 27 parts of a mixture of isomers of diisopropylbenzene with 3 parts of crystal violet lactone and 1 part of N-benzoylleuco-

methylene blue is encapsulated.

150 parts of chloroform and various copolymers are used as wall materials for the encapsulation. The copolymers used, the capsule diameter and copying intensity obtained may be seen in the following Table 1. In these tests the storage test is made more stringent by increasing the storage period from sixteen hours to twenty-four hours at 95°C. Capsule diameters are determined microscopically in each case.

The following abbreviations are used in the Table:

BMA = butanediol monoacrylate acetylacetate

MM = methyl methacrylate

AM = acrylamide

Nas = sodium sulfoethylmethacrylate

CD = capsule diameter in microns (yield in each case more than 98%)

CI = copying intensity (ratings 5 to 1) at room temperature (i) and after twenty-four hours at 95°C (ii)

+ = comparative results with dichlorodiphenyl as developer liquid mixed with mineral spirit in the ratio 9:1 in an amount as in Example 1(a).

Table 1

Wall Material							
BMA	MM	AM	Nas	CD	CI(i)	CI(ii)	
30	58	12	0.5	4-5	5	2	
36	52	12	0.5	4-5	5	3	
44	44	12	0.5	6-7	5	4	
58	39	12	0.5	6-8	5	5	
+44	44	12	0.5	8-10	5	1	

The yield is determined by filtering the dispersion through a sieve of 160  $\mu$  mesh. The amount of dye and core material remaining in the dispersion is determined gravimetrically and compared with the residue on the sieve.

Only moderate storability is obtained with a mixture of chlorodiphenyl and mineral spirit (9:1).

#### EXAMPLE 4

As described in Example 3 further copolymers are used as wall materials for the encapsulation of the solvents and dye-forming components used.

The amount of chloroform in each case is raised to 180 parts and 198 parts and optionally 3 parts of isopropanol is used if the solubility of the copolymer in the solvent mixture is not sufficient. The results obtained are given in Table 2 in which the following additional abbreviations are used:

PWM = parts of wall material (40%)

SMA = sodium methacrylate

AA = acryl acid

VS = vinylsulfonic acid

Table 2

Wall material			PWM CD CI(i) CI(ii)				
BMA	MM	AM					
42	42	16	—	60	7-8	5	4-5
41	41	18	0.25 Nas	60	7-9	5	4-5
42	42	16	0.5 SMA	60	6-8	5	4-5
41	41	18	0.5 AA	60	7-8	4-5	4-5
42	41	16	0.5 VS	60	6-8	5	5
42	42	16	0.25 Nas	75	7-10	4-5	4-5
42	42	16	0.25 Nas	90	7-10	5	5
42	42	16	0.25 Nas	110	10-14	5	5

(a) As described in Example 1 a mixture of 27 parts of diethylhexyl phthalate and 40 parts of p-diisopropylbenzene is encapsulated instead of p-diisopropylbenzene. The sodium salt of a polyacrylic acid (K value in 1% aqueous solution 210 at a pH of 7.0) is added instead of polyvinylpyrrolidone. A stable dispersion is formed in a yield of more than 98% with a capsule diameter of from 7 to 8 microns. Papers coated therewith can be stored in the sixteen-hour test without loss of copying efficiency at up to 95°C and give a copying intensity of rating 4 to 5.

(b) Instead of the p-diisopropylbenzene of Example 1 a mixture of 15 parts of a terphenyl (mixture of various substituted diphenylbenzenes) and 52 parts of p-diisopropylbenzenes is encapsulated as developer liquid for dye-forming components.

A stable dispersion is formed with capsules of the diameter 5 to 7 microns.

Papers coated therewith can be stored in the sixteen-hour test at 95°C without undergoing change and give a copying intensity of rating 4 to 5.

#### EXAMPLE 5

A solution of 19 parts of gelatin in 90 parts of water of a pH of 5.5 is prepared at 55°C in a glass beaker holding 800 parts. While mixing with an impeller having a disc blade a suspension of 2.4 parts of crystal violet lactone and 0.8 parts of N-benzoylleucomethylene blue in 30 parts of commercial n-dodecylbenzene and 23 parts of diisopropylbenzene is emulsified in at 55°C until a droplet size of from 8 to 10 microns has been formed. Then a solution of 19 parts of gum arabic in 80 parts of water is added within six minutes at 55°C (pH = 4.7).

The dispersion is placed in a beaker holding 1000 parts and while stirring it is adjusted to pH 5.35 with normal caustic soda solution. Then at 55°C 300 parts of water at 55°C is allowed to flow in at 55°C in twenty minutes, the emulsion is adjusted with 0.1N acetic acid to pH 4.5 in about fifteen minutes and stirred for another twenty minutes. After 3.6 parts of formaldehyde solution (37%) has been dripped in the whole is cooled in fifty minutes to 5°C and slowly adjusted to pH 9.5 with 0.2N caustic soda solution. Six hours later the capsule walls are hardened. The dispersion has a total

solids content of about 19% and does not settle out. The capsules have a diameter of about 8 microns.

- 5 Paper coated with the dispersion gives a copying intensity of rating 5 under the conditions described above both at room temperature and also in the case of samples stored for sixteen hours at 80°C and 95°C.

#### EXAMPLE 6

- 10 A core material consisting of 37 parts of n-dodecylbenzene and 30 parts of p-diisopropylbenzene is encapsulated with 3 parts of 3-methyl-bis-naphthospiropyran according to Example 1.

- 15 The copying intensity and storage at elevated temperature are determined according to Example 2.

- The stability to light of the typed paper is determined by using a quartz ultraviolet lamp (HANAU model Q 500 with an 840 watt ultraviolet burner). The distance from the burner is 20 cm. After an exposure time of five minutes the paper prepared according to Example 6 shows virtually no discoloration where-  
25 as a paper in which the solvent mixture of n-dodecylbenzene and diisopropylbenzene has been replaced by dichlorodiphenyl shows marked discoloration. Copying tests carried out after exposure give rating 5 for Example 6 and rating 2 for the dichlorodiphenyl sample.

#### WHAT WE CLAIM IS:-

1. Microcapsules containing as microencapsulated material at least one dye and a water-immiscible liquid which comprises one or more monoalkyl-substituted benzenes of which the alkyl group contains at least five carbon atoms or one or more polyalkyl-substituted benzenes of which the alkyl groups are, each independently, linear or branched and contain, each independently, from one to eighteen carbon atoms with the alkyl groups containing a combined total of at least five carbon atoms.

2. Microcapsules as claimed in claim 1 wherein the water-immiscible liquid consists of a monoalkylbenzene of which the alkyl group contains from ten to eighteen carbon atoms.

3. Microcapsules as claimed in claim 1 or claim 2 wherein the water-immiscible liquid is pure or technical dodecylbenzene.

- 50 4. Microcapsules as claimed in claim 1 wherein the water-immiscible liquid consists of a diisopropylbenzene, triisopropylbenzene or a polyethylenebenzene having at least three ethyl groups.

5. Microcapsules as claimed in claim 1 wherein the water-immiscible liquid consists of a mixture in the ratio by weight of from 1:5 to 5:1 of:

diisopropylbenzene and dodecylbenzene; triisopropylbenzene and dodecylbenzene; or triisopropylbenzene and a polyethylbenzene having at least three ethyl groups. 55

6. Microcapsules as claimed in claim 1 wherein the water-immiscible liquid consists of a mixture of two or more monoalkylbenzenes of which the alkyl radical contains from eight to fourteen carbon atoms, said mixture containing the individual alkylbenzenes in amounts of not more than 35% by weight. 60

7. Microcapsules as claimed in any of claims 1 to 6 wherein additional solvent is added to the alkylated benzenes in an amount of up to 25% by weight. 65

8. Microcapsules as claimed in any of claims 1 to 7 and containing a high boiling point aliphatic hydrocarbon, a diphenylbenzene, a diphenyl, a terphenyl, a phthalic ester, an indan, a tetralin, a polynuclear aromatic or an alkylated polynuclear aromatic as an additional solvent. 70 75

9. Microcapsules as claimed in any of claims 1 to 8 wherein the wall material consists of a copolymer of: from 20 to 70% by weight of methyl methacrylate; 80

from 20 to 70% by weight of an acetylacetate of an acrylate or methacrylate of a diol of two to eight carbon atoms;

from 0 to 30% by weight of acrylamide; 85

from 0 to 30% by weight of acrylic or methacrylic acid;

from 0 to 30% by weight of vinylpyrrolidone;

from 0 to 30% by weight of vinylsulfonic acid or a salt thereof; and

from 0 to 30% by weight of 2-sulfoethylmethacrylate or a salt thereof. 90

10. Microcapsules substantially as described in any of the foregoing Examples.

11. Copying paper comprising a substrate having on a surface thereof a coating comprising microcapsules as claimed in any of claims 1 to 10. 95

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